



Cobalt clusters decorated $\text{Co}_x\text{Mn}_{1-x}\text{O}$ nanocomposites for improving the efficiency of syngas to lower olefins with lower CO_2 emission

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ARTICLE INFO

Keywords:
Lower olefins
Fischer-Tropsch synthesis
Carbon usage
 CO_2 selectivity
Co cluster

ABSTRACT

Fischer-Tropsch synthesis has long been the most important means to convert non-fossil resources to high value-added products, i.e., lower olefins. However, the selectivity tends to be low. In the past decades, the efforts devoted to improving the selectivity toward lower olefins have been rewarded, but the selectivity toward undesired CO_2 is overlooked and normally over 40%, resulting in a poor carbon usage effectiveness. Here, we describe $\text{Co}_x\text{Mn}_{1-x}\text{O}$ nanocrystals to achieve a high selectivity (65.4%) toward lower olefins and a remarkably low CO_2 selectivity of only 13.7%. Such superior performance is due to the formation of stable Co^0 clusters (<1 nm) as active sites, which facilitate the activation of CO and weaken the C-C coupling to generate lower olefins, and suppress water-gas shift reaction to minimize CO_2 emission. Our work represents a conceptual advance to the design of highly efficient catalysts for superior lower olefins selectivity by taking CO_2 into account.

1. Introduction

Lower olefins ($\text{C}_2\text{--C}_4$) are of pivot significance as building blocks in chemical industry for the manufacture of a variety of products. The traditional methods for the production of olefins require the use of naphtha, diesel, and other petroleum products as precursors [1,2]. The growing demands for olefins and dwindling petroleum supplies compel the development of technologies for the generation of olefins from nonpetroleum resources [3]. Fischer-Tropsch synthesis (FTS) represents the most reliable human endeavor to convert syngas, which could be derived from biomass, coal, and natural gas, producing clean fuels and high-value-added chemicals especially lower olefins [4–7]. FTS is essentially a polymerization reaction that takes place on the surface of various catalysts, generating products that follow the traditional Anderson-Schulz-Flory (ASF) distribution featured with low selectivity [8]. In the past decades, there have been numerous studies on breaking the ASF restriction in FTS to render high selectivity towards desired products, for example, lower olefins [9–13].

Recently, notable achievements have been made in selective conversion of syngas towards lower olefins (FTO) through the delicate design of the structures of the catalysts. For example, de Jong and coworkers reported a Fe-based catalyst promoted by sulfur and sodium to

achieve up to 61% selectivity for $\text{C}_2\text{--C}_4$ olefins, which is close to the upper limit predicted by the ASF theory [14]. Zhong and coworkers also obtained up to 61% selectivity for lower olefins in syngas conversion through the manipulation of the exposed active facets of Co_2C nanoprisms [15]. Bao and coworkers described a remarkably high selectivity of 80% for lower olefins at 400 °C that breaks the theoretical ASF limit by using OX-ZEO relay catalysts [16]. These efforts are encouraging, however, the calculation of the selectivity in previous studies excludes the fraction of CO_2 , which normally accounts for around 45% in terms of carbon number and poses great challenges for efficient carbon usage. Very recently, Ding and coworkers reported a variation of the micro-environment of the active iron carbide catalyst by using a hydrophobic shell, which effectively reduced the retention time of water on the catalyst surface and suppressed the water gas shift reaction, resulting in a significant decrease of the CO_2 selectivity of only around 10% with an olefin yield of 36.6% [17]. It is thus highly desired to achieve both high olefin yield and low CO_2 selectivity, for the elevation of carbon efficiency in syngas conversion and the contribution to the carbon emission reduction on a global scale.

Previous studies have concluded that the Co_2C nanoprisms generated during the reaction are the active sites for the conversion of syngas to lower olefins, where the presence of Na element facilitates the formation

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of Co_2C nanoprisms from CoMn oxides catalyst. Nevertheless, the Co_2C phase possesses high water-gas-shift reaction activity, resulting in a high CO_2 emission in the FTS process. In this study, we report a surface reconstruction strategy to manipulate the catalytic performance of a series of CoMn oxides nanocomposite catalysts in FTS. An illustration of the surface reconstruction of CoMn oxide nanocomposite to generate Co^0 clusters during reduction treatment and FTS reaction is presented in Fig. 1. Remarkably, the optimal catalyst achieved high selectivity towards lower olefin (65.4%), and low CO_2 selectivity of only 13.7%. Several ex-situ characterization techniques reveal that the Co^0 clusters are the key active sites for such prominent catalytic performance. Theoretical calculations suggest that compared to normal Co metal, the Co^0 clusters is thermodynamically less favored for the formation of Co_2C phase, thus suppressing the CO_2 formation (Fig. 1). Such surface reconstruction represents an effective strategy to boost the catalytic performance of FTS catalysts, providing a conceptual advance to achieve higher carbon usage effectiveness by reducing CO_2 emission.

2. Experimental

2.1. Materials synthesis

The mixture of $\text{Co}(\text{acac})_2$ and $\text{Mn}(\text{acac})_3$ (the mole ratio of Co to Mn is from 10/1–1/7) was dispersed in benzylamine and heated to 220°C with a continuous stirring. The reaction mixture was cooled to room temperature after 2 h. The precipitate was then collected by centrifugation, followed by washing with ethanol and drying at 60°C in a vacuum drying oven for 6 h. The as-synthesized sample was denoted as Co_xMn_y (x/y is from 10/1–1/7).

CoO nanocrystals were synthesized by thermal decomposition of $\text{Co}(\text{acac})_2$ (7.6 mmol) in benzylamine (560 mmol) at 200°C for 2 h. The precipitate was then collected by centrifugation, followed by washing with ethanol and drying at 60°C in a vacuum drying oven for 6 h. The obtained sample was denoted as CoO .

To synthesize MnO nanocrystals, a similar procedure was used. A mixture of $\text{Mn}(\text{acac})_3$ (7.6 mmol) and benzylamine (560 mmol) were placed in the flask. The reaction was heated at 200°C for 2 h. After cooling down to room temperature, the product was precipitated with the addition of ethanol and collected by centrifugation. Then the product was reduced in H_2 at 400°C for 3 h. The obtained sample was denoted as MnO .

Before performance testing, all the catalysts were modified with Na promoter by impregnation Na_2CO_3 aqueous solution. 1.0 g Co_xMn_y nanocrystals and a certain amount of Na_2CO_3 powder were dispersed in 100 ml mixture solution of deionized water and ethanol (ratio of 1:1).

After ultrasonicated for 2 h, followed by evaporation in a rotary evaporator at 90°C for 1 h ($50\text{--}90^\circ\text{C}$ with heating rate of $5^\circ\text{C}/30\text{ min}$) under vacuum. The obtained sample was dried at 120°C for 12 h. The Na content was 0.4 wt%.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained by a Bruker D8 powder diffractometer using $\text{Cu-K}\alpha$ radiation operated at 40 kV and 40 mA and a Vantec-1 detector.

The size and morphology of samples were determined using a FEI Tecnai G20 transmission electron microscope operated at 200 kV and a Hitachi SU8000 field emission scanning electron microscope at an accelerating voltage of 15 kV. The particle size distribution for samples was calculated by more than 200 nanoparticles.

Ex-situ X-ray Photoelectron Spectroscopy (XPS) measurements were conducted by a VG Multilab 2000 photoelectron spectrometer equipped with $\text{Al-K}\alpha$ radiation under vacuum at 2×10^{-6} Pa. All binding energies were calibrated using the C 1 s peak (284.6 eV) of the surface adventitious carbon. The exposure to H_2 or syngas was done in a chamber. The solid samples were reduced at 300°C in a H_2 atmosphere (0.1 MPa) for 5 h. The reduced samples were loaded into the test chamber inside a glove box, and then the XPS data of $\text{Co}_1\text{Mn}_3\text{-R}$ was collected. For investigate the FTS reaction on the Co_1Mn_3 catalysts, the chamber was vacuumed again to eliminate the excess hydrogen, and syngas ($\text{H}_2/\text{CO} = 1$, 0.1 MPa) was introduced at 250°C for 2 h and 50 h. Then, the XPS spectra was recorded following the above-mentioned procedures.

The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the samples were collected at the Singapore Synchrotron Light Source (SSLS) center, where a pair of channel-cut Si (111) crystals was used in the monochromator. The storage ring was working at the energy of 2.5 GeV with average electron current of below 200 mA.

Hydrogen temperature-programmed desorption (H_2 -TPD) experiment was conducted on Zeton Altamira AMI-300 unit. Co_xMn_y Catalysts were pretreated in flowing argon at 373 K for 1 h, and reduced in flowing hydrogen at 573 K for 5 h while the temperature increased from 373 to 573 K at a ramping rate of 10 K min^{-1} . The sample was then cooled to 373 K under hydrogen flow and purged with argon at 373 K for 1 h to remove physisorbed hydrogen species. The temperature was then increased slowly from 373 K to 773 K, and held under flowing argon to desorb the remaining chemisorbed hydrogen. A TCD detector was used to register the desorption signal until it returned to the baseline. The TPD spectrum was integrated and the amount of chemisorbed hydrogen was determined by comparing with the mean areas of calibrated

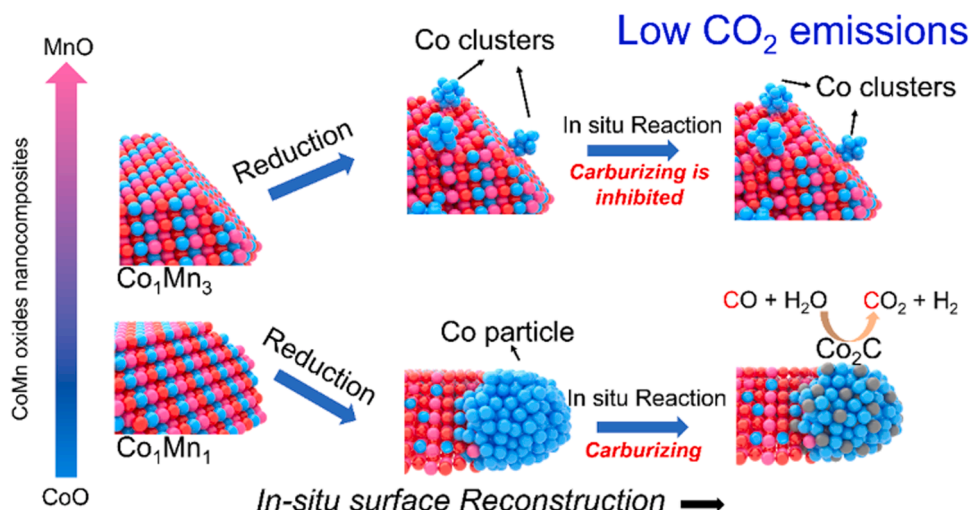


Fig. 1. Schematic models of the evolution of active phase in Co_1Mn_1 (below) and Co_1Mn_3 (above) catalyst.

hydrogen pulses.

The samples' compositions were analyzed by the inductively coupled plasma optic emission spectrometer (ICP-OES, Varian 720).

2.3. Catalytic reaction

Fischer-Tropsch synthesis was performed in a fixed-bed reactor with 1/4 in. inner-diameter stainless-steel tube. 0.1 g catalyst was diluted with 0.3 g quartz sand prior to testing. After reduction at 573 K by pure H_2 (8 SL $g_{cat}^{-1} h^{-1}$) for 5 h, the catalyst was cooled to 373 K in flowing H_2 before introduction of syngas ($H_2/CO/N_2 = 45/45/10$, N_2 as internal standard). The gas hourly space velocity (GHSV) was maintained as 4 SL $g_{cat}^{-1} h^{-1}$, while the pressure was maintained at 0.1 MPa. The reaction temperature was then ramped slowly to 523 K. During reaction, the permanent gases (H_2 , CO , CO_2) and light alkanes in the effluent of the reactor were monitored by an online gas chromatograph (Agilent 7890B, equipped with molecular sieves, Plot-Q and Al_2O_3 capillary column). CO_2 , H_2 , CO , and N_2 were detected by thermal conductivity detector (TCD), while hydrocarbons were detected by Flame ionization detector (FID). The liquid products including oil and water were condensed in a cold trap (273 K). The oil products were analyzed using an Agilent 6890 N GC with a FID detector and a HP-5 column. The aqueous fraction was analyzed using an Agilent 4890 GC equipped with a FID detector and a HP-Innowax column. The product selectivity was calculated based on the carbon balance.

2.4. DFT calculations

Density functional theory (DFT) calculations were performed using generalized gradient approximation Perdew-Burke-Ernzerhof (PBE) functional [18] and projector-augmented wave (PAW) method [19] as implemented in Vienna ab initio simulation package (VASP) [20]. Second order Methfessel-Paxton electron smearing scheme ($\sigma = 0.2$ eV) was used because of the metallic properties of Co and Co_2C . Plane-wave kinetic energy cutoff of 400 eV was applied for the spin polarization calculations with the energy and force convergence criteria of 10^{−5} eV and 0.03 eV/Å, respectively. The bulk structures of hexagonal closely packed Co and orthorhombic Co_2C were optimized with Monkhorst-Pack k-points of $14 \times 10 \times 10$ and $16 \times 16 \times 10$. The clusters in different sizes were truncated from the bulks. A thick vacuum of ca. 15 Å was added to each direction for screening the lateral interaction. The transition state (TS) structures were located by combining the climbing-image nudge elastic band (cNEB) and quasi-Newton minimizing techniques. Frequency calculations were used to confirm the TS structure with only one imaginary frequency.

3. Results and discussion

3.1. Co_xMn_y oxides nanocomposites for FTO

A group of Co_xMn_y oxide nanocomposites with different Co/Mn contents was synthesized via the one-pot thermal decomposition of a mixture of $Co(acac)_2$ and $Mn(acac)_3$ with different ratios in benzylamine

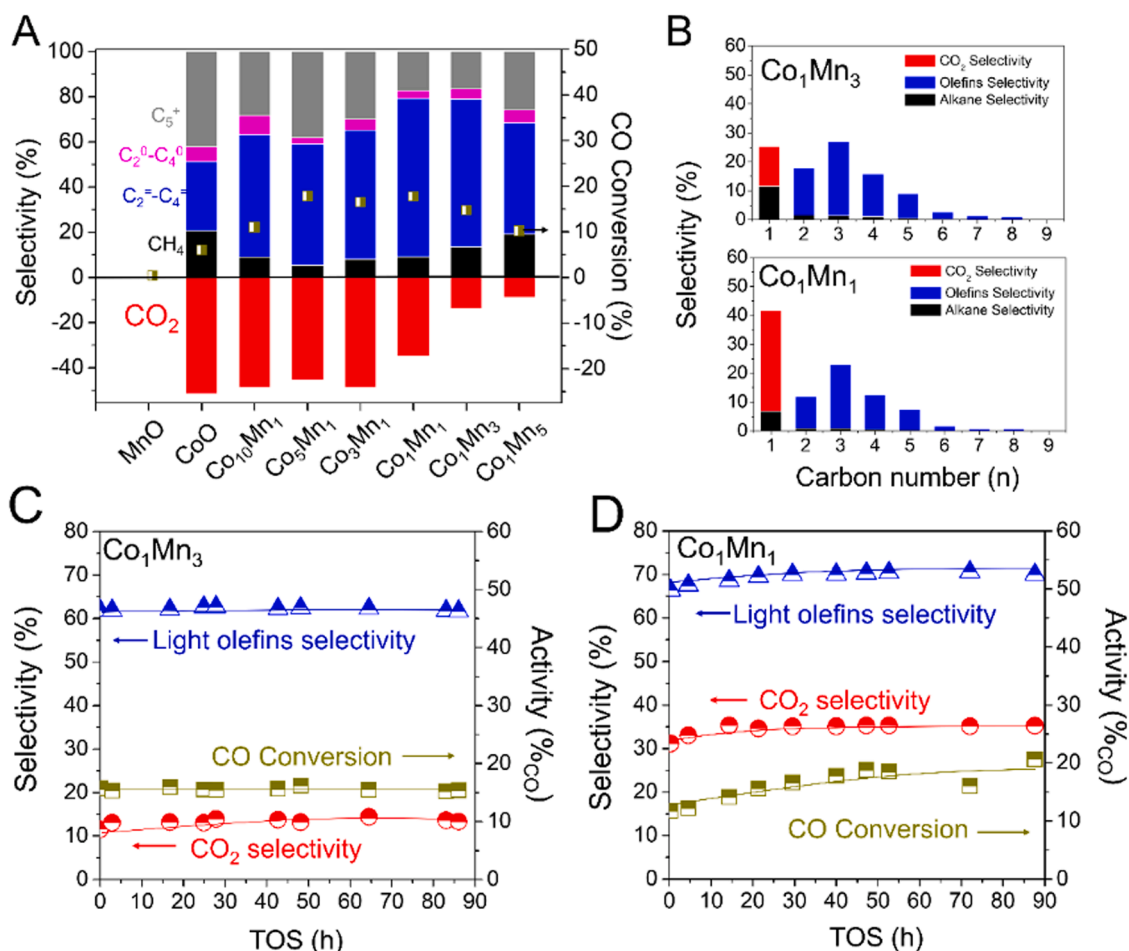


Fig. 2. Catalytic performance of different CoMn oxide nanocomposites catalysts. (A) Product distribution and CO conversion of different Co_xMn_y catalysts. (B) Detailed product distribution (including CO_2) over Co_1Mn_3 and Co_1Mn_1 catalysts. A stability test of (C) Co_1Mn_3 catalyst and (D) Co_1Mn_1 catalyst. Reaction condition: 250 °C, 0.1 MPa, $H_2/CO = 1$.

at 220 °C, followed by the modification of Na promotor. The subscript x and y in Co_xMn_y oxides represent the molar ratio of Co to Mn, which were determined by ICP-OES (Table S1). For blank comparison, pure CoO and MnO nanocrystal samples were also prepared. These samples were reduced at 300 °C with pure H_2 , and then used for fixed-bed FTS with a H_2/CO ratio of 1:1 under the pressure of 0.1 MPa at 250 °C. Results in Fig. 2A and Table S2 show that CoO displays a low CO conversion of 6.0%, a light olefin selectivity of 30.6%, and a high CO_2 selectivity of around 46.9%, whereas MnO shows no activity of FTS.

For all Co_xMn_y oxide nanocomposites, the CO conversion is elevated to around ~15%. Specifically, $\text{Co}_{10}\text{Mn}_1$ exhibits an improved light olefin selectivity of 54.1% and a CO_2 selectivity of around 48.7%. As the increase of Mn fraction, both Co_5Mn_1 and Co_3Mn_1 demonstrate light olefin selectivity around 55.0%, but the CO_2 selectivity is still as high as above ~45%. Interestingly, as the further increase of Mn fraction, the Co_1Mn_1 catalyst shows a much improved light olefins selectivity of around 70.0% and an obviously reduced CO_2 selectivity of 34.9%. Surprisingly, the Co_1Mn_3 catalyst exhibits a light olefins selectivity of 65.4% and a remarkably low CO_2 selectivity of only 13.7%. More importantly, the products are mainly α -olefins, with olefin/paraffin molar ratio of 13.9 in the C_2^+ hydrocarbons.

For the Co_1Mn_5 catalyst with a higher Mn content, the CO_2 selectivity is further reduced to 9.5%, but the methane selectivity increases to 19.0%, the CO conversion decreases to 10.2%, and the lower olefins selectivity decreases to 49.2%. The improved methane selectivity is possibly related to the size of the Co nanoparticles on the surface of the catalyst. [21] Among these catalysts, the Co_1Mn_3 catalyst represents an unprecedented achievement of high selectivity towards light olefins and low selectivity towards CO_2 .

The overall product distributions including CO_2 are presented in Fig. 2B. Compared to Co_1Mn_1 , Co_1Mn_3 demonstrates a much lower CO_2 selectivity without affecting the selectivity toward lower olefins. The difference in the catalytic performances between Co_1Mn_3 and Co_1Mn_1 was further evaluated in the continuous FTO reaction over 90 h. As shown in Fig. 2C and D, the CO conversion and product distribution remain stable with time on steam for Co_1Mn_3 samples. The CO conversion of Co_1Mn_1 increases with time on steam. This change of CO conversion should be due to the phase change of Co_1Mn_1 during the reduction and reaction. [15].

Moreover, temperature effect on catalytic performance of Co_3Mn_1 and Co_1Mn_1 catalyst are investigated, as shown in Table S3. The results show that CO conversion increased with the reaction temperature increasing, but the CO_2 and CH_4 selectivity increased significantly. Specifically, for Co_1Mn_3 , the selectivity toward undesired CO_2 is suppressed to be only 13.7% and the selectivity toward lower olefins

remains at ~60% by taking CO_2 into account, during the 90 h continuous experiment. These differences in catalytic performance between Co_1Mn_3 and Co_1Mn_1 imply that there should be different active sites involved in the FTS reaction. Previous studies have suggested that for Co_1Mn_1 , the generated Co_2C phase should act as the active site for FTS reaction [15,22]. Intriguingly, the active site in Co_1Mn_3 needs further elucidation.

3.2. Catalysts structure and structure evolution

We started our investigation from examining the crystalline structures of these samples by XRD. Fig. 3A shows that for CoO, the diffraction peaks at 36.5°, 42.4°, and 61.5° are attributed to the (111), (200), and (220) planes of the fcc CoO (Fm3m, $a = 4.26 \text{ \AA}$, JCPDS 48–1719). For MnO, the diffraction peaks at 34.9°, 40.5°, and 58.7° are attributed to the (111), (200), and (220) planes the fcc MnO (Fm3m, $a = 4.44 \text{ \AA}$, JCPDS 78–0424). With respect to the Co_xMn_y oxide nanocomposites, the diffraction peaks shift gradually between the peaks of CoO and MnO as the molar ratio of Co/Mn varies, while maintaining the fcc phase structure. These results suggest a uniform crystalline structure of the Co_xMn_y oxide nanocomposites regardless of the metal fraction from $\text{Co}_{10}\text{Mn}_1$ to Co_1Mn_3 . The further increase of Mn content results in the formation of Mn_3O_4 (Fig. S1 for the XRD patterns of Co_1Mn_5 sample).

TEM images of Co_xMn_y oxide nanocomposites with different Co/Mn contents show nanocrystals with size of 10–20 nm and excellent dispersion and uniformity (Fig. S2). Moreover, a high-angle annular dark-field (HAADF) image of the representative Co_1Mn_1 sample (Fig. S3a) shows the uniform distribution of octahedron nanocrystals. The corresponding EDX mappings of Co_1Mn_1 (Fig. S3b-d) confirm the uniform distribution of both Co and Mn elements in the nanocrystals. These Co_xMn_y oxide nanocomposites show similar morphologies but dramatically different catalytic performances, especially different CO_2 selectivity, presumably indicating distinct structural evolution during reduction and FTS reaction.

The reduction behavior of these Co_xMn_y oxide nanocomposites were examined by H_2 -TPR. Fig. 3B shows that all samples except MnO exhibit two distinct peaks, i.e., a peak from 260 to 420 °C ascribing to the reduction of the surface Co_3O_4 species, and a peak from 420 to 650 °C attributing to the reduction of Co^{2+} to Co^0 [23]. The obvious shift of both peaks to higher temperature suggests that the reduction becomes more difficult as the increase of Mn content. For pure MnO, reduction signal is barely observed in Fig. 3B.

After reduction, these samples, with new names containing a suffix of -R, were re-characterized by XRD. Fig. S4 shows that from the sample of $\text{Co}_{10}\text{Mn}_1$ -R to Co_1Mn_1 -R, both diffraction peaks of $\text{Co}_x\text{Mn}_{1-x}\text{O}$ and metal

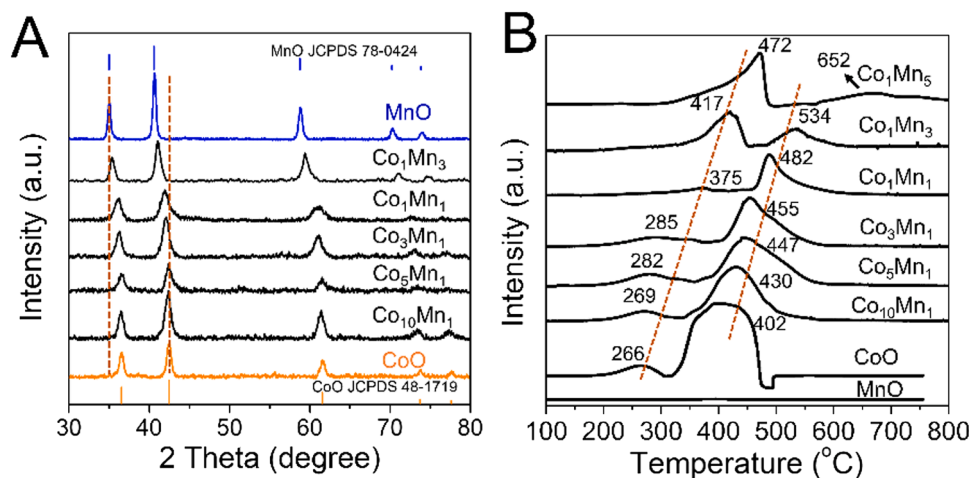


Fig. 3. Structure of CoMn oxides nanocomposites. (A) XRD pattern of different Co_xMn_y catalysts. (B) H_2 -TPR profiles of different Co_xMn_y oxides nanocomposites, pure CoO and MnO sample.

Co are observed, but with decreasing Co signals. This result implies that crystalline Co nanoparticles are generated after the reduction process and formed from the surface of the CoMn oxides, generating $\text{Co}_x\text{Mn}_{1-x}\text{O}$ nanocomposites. Moreover, the diffraction peaks of $\text{Co}_x\text{Mn}_{1-x}\text{O}$ gradually shift to smaller angle during the reduction process. These results from H_2 -TPR and XRD are consistent that as the decrease of Co content in the Co_xMn_y oxide nanocomposites, the reduction of CoMn oxide to form Co metal with long-range order becomes more difficult. In contrast, for the Co_1Mn_3 -R catalyst with a high lower olefins selectivity and a lower CO_2 selectivity, no metal Co signal could be observed, suggesting that Co nanoparticles are not generated after reduction. The active surface sites of the Co_1Mn_3 -R catalyst need further characterizations, which will be presented later.

3.3. Structure analysis of spent catalysts

After the FTS reaction, these catalysts were given new names containing a suffix of -S and were examined by XRD for the third time. Fig. S5 shows that from $\text{Co}_{10}\text{Mn}_1$ -S to Co_1Mn_1 -S, both diffraction peaks of $\text{Co}_x\text{Mn}_{1-x}\text{O}$ and Co_2C are observed. The generation of Co_2C is because

of the carbonization of metal Co during FTO reaction, which has been demonstrated in previous studies [23,24]. Interestingly, in the Co_1Mn_3 -S sample, the Co_2C phase is not present. These results are consistent with the fact that the signal of metal Co is not observed in Fig. S4 and further verify our hypothesis that the structural evolution during reduction and FTS reaction of Co_1Mn_3 is different from that of other Co_xMn_y samples.

In the following sections, we will explore the difference of the two samples, i.e., Co_1Mn_3 and Co_1Mn_1 as the representative of other Co_xMn_y samples, to elucidate the structural origin of the superior catalytic performance of Co_1Mn_3 . The structural difference between the Co_1Mn_3 and Co_1Mn_1 was confirmed by HRTEM characterization on the spent samples after FTO reaction. For Co_1Mn_3 -S, Figs. S6a to 6c show the uniform distribution of Co elements in the $\text{Co}_x\text{Mn}_{1-x}\text{O}$ nanocomposite, while Co_2C is not observed. For Co_1Mn_1 -S, Figs. S6d to 6f show an apparent migration of the Co species to the surface of the $\text{Co}_x\text{Mn}_{1-x}\text{O}$ nanocomposite to form Co_2C moiety. The Co_2C nanoprisms contribute to the high C_{2-4} selectivity and CO_2 selectivity, which is consistent with previous study [15].

In order to reveal the fine atomic structure, X-ray adsorption near-edge structure (XANES) and extended X-ray adsorption fine structure

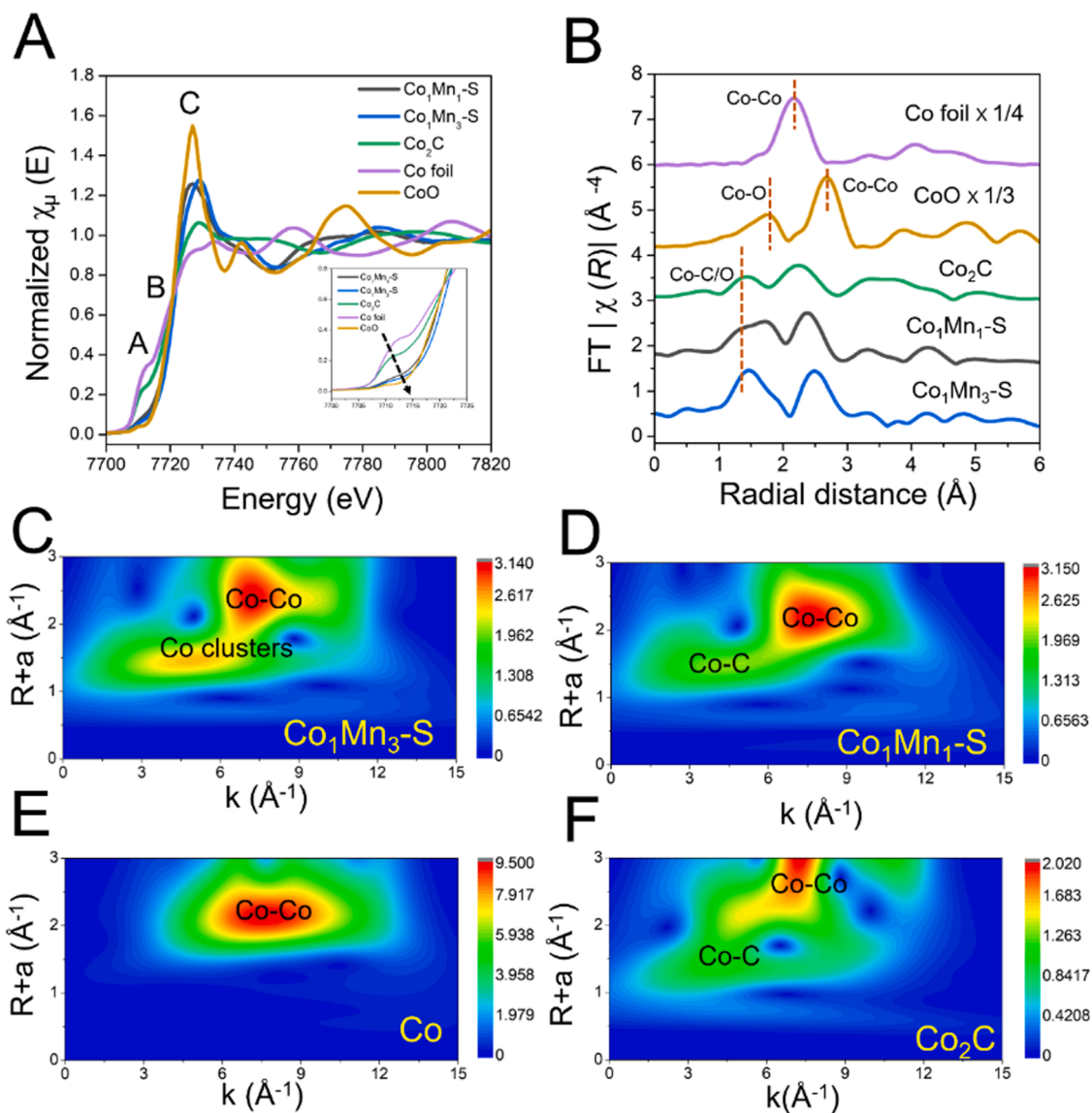


Fig. 4. XAS characterization of spent CoMn oxides nanocomposites. (A) Co K-edge XANES spectra of different Co_xMn_y -S samples and reference of Co foil, Co_2C and CoO. (B) Fourier transform spectra for the used catalyst and reference of Co foil and CoO sample. (C)-(F) Wavelet transforms for Co_1Mn_3 -S, Co_1Mn_1 -S, Co foil and Co_2C , respectively.

(EXAFS) characterizations were performed on $\text{Co}_1\text{Mn}_3\text{-S}$ and $\text{Co}_1\text{Mn}_1\text{-S}$ samples after FTS reaction. The Co K-edge XANES spectra are shown in Fig. 4A, with Co foil and standard CoO and Co_2C as references. The spectra contain a weak pre-edge peak A, a shoulder peak B on the rising edge, and a sharp white-line peak C. The position of peak A is related to the valence state of the element, where the peak at higher energy implies a higher oxidation state [25]. The valences of Co in both $\text{Co}_1\text{Mn}_3\text{-S}$ and $\text{Co}_1\text{Mn}_1\text{-S}$ are slightly lower than +2, suggesting the reduction of Co element after the FTO reaction. Moreover, the peak A of $\text{Co}_1\text{Mn}_1\text{-S}$ resembles that of Co_2C , confirming that the Co_2C is the active site [26].

The FT-EXAFS spectra of these samples are shown in Fig. 4B. The $\text{Co}_1\text{Mn}_1\text{-S}$ sample shows signals that are very close to Co_2C . Interestingly, the $\text{Co}_1\text{Mn}_3\text{-S}$ sample exhibits a peak at the R distance of 1.5 Å, which is between the signal of Co-C/O of Co_2C at 1.4 Å and the signal of Co-O of CoO at 1.8 Å. This peak is speculated to be from a new Co structure that is different from Co_2C and CoO. Such information is also validated by the data fitting (Fig. S7 and S8) and the structural parameters extracted from the data fitting in Table S4.

Moreover, the wavelet transforms (WT) contour plots at the first and second shells of the $\text{Co}_1\text{Mn}_3\text{-S}$ and $\text{Co}_1\text{Mn}_1\text{-S}$ samples are shown in Fig. 4C and D. It is obvious that both samples exhibit good metallic characters, showing a Co-Co shell at around 6.5 Å^{-1} which is close to

that of Co foil (Fig. 4E). Compared with the Co foil, the $\text{Co}_1\text{Mn}_3\text{-S}$ sample could be well fitted to Co clusters, which will be verified later. For $\text{Co}_1\text{Mn}_1\text{-S}$, it is observed that a Co_2C phase with a Co-C/O shell at 4.2 Å^{-1} (Fig. 4F) appears.

3.4. Surface reconstruction of Co_1Mn_3 and Co_1Mn_1 catalyst

The Co_1Mn_3 sample at different stages, i.e., the fresh Co_1Mn_3 , the reduced $\text{Co}_1\text{Mn}_3\text{-R}$, and two samples at different FTS reaction time $\text{Co}_1\text{Mn}_3\text{-S-2 h}$ (after reaction of 2 h) and $\text{Co}_1\text{Mn}_3\text{-S-50 h}$ (after reaction of 50 h), were further examined by ex-situ XPS characterization in order to probe the active site involved. Fig. 5A shows the evolution of the Co 2p spectra at different stages. For the fresh Co_1Mn_3 , the peaks at 781.1 and 780.2 eV could be attributed to the characteristic signals of Co^{2+} and Co^{3+} , respectively [27], whereas the peak at 782.4 eV could be assigned to the Co^{2+} in hydroxide. After the reduction treatment at 300 °C for 5 h, the $\text{Co}_1\text{Mn}_3\text{-R}$ exhibits a new peak at 778.2 eV, ascribing to the generation of Co^0 clusters on the surface of the catalyst [28]. This Co^0 signal preserves in both of the two $\text{Co}_1\text{Mn}_3\text{-S-2 h}$ and $\text{Co}_1\text{Mn}_3\text{-S-50 h}$ samples after FTS reaction. This result complies with the conclusion from the EXAFS experiments that a new Co^0 cluster phase appears in Co_1Mn_3 , affording key role in the FTS reaction. These Co^0 clusters are

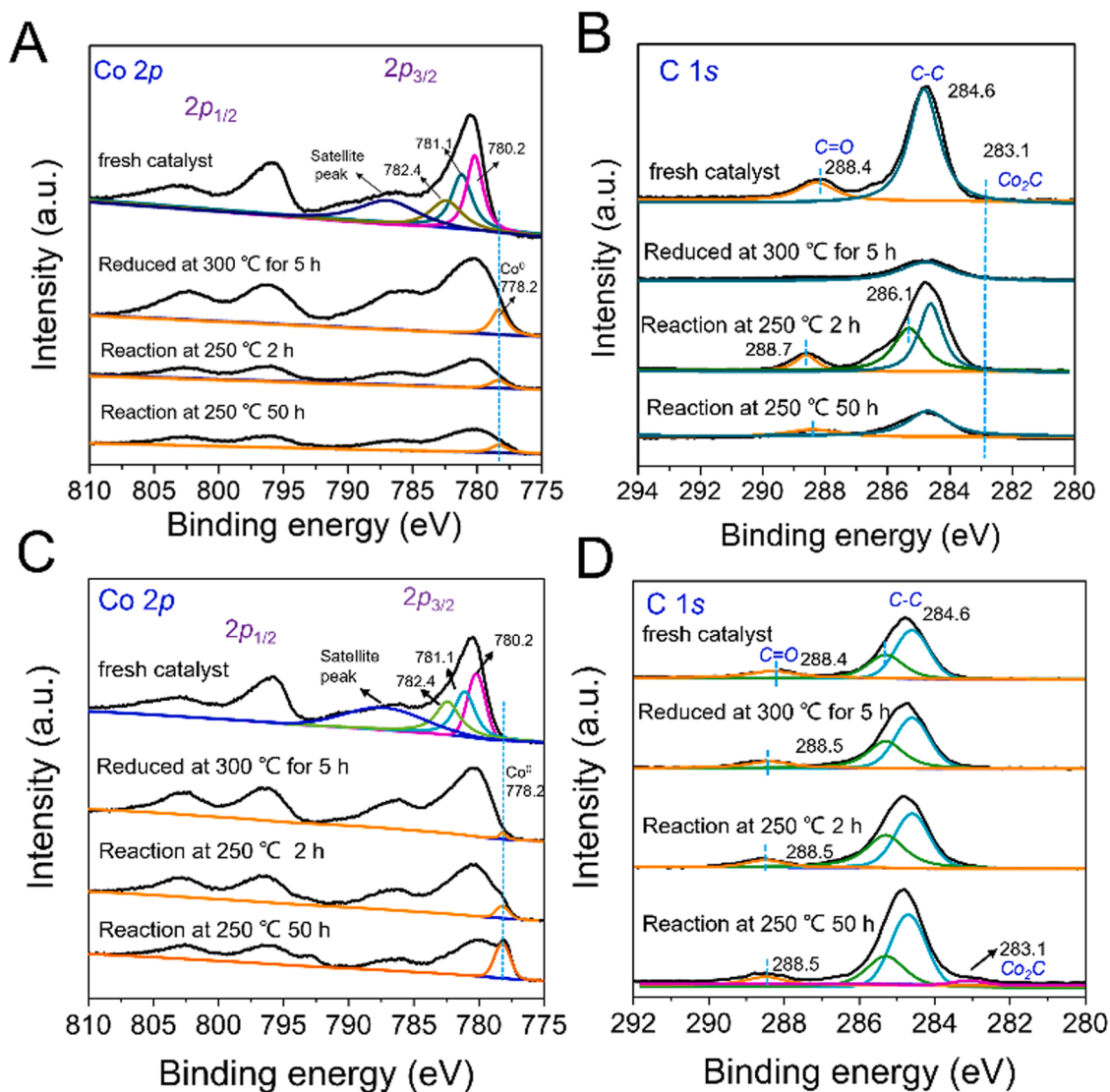


Fig. 5. Ex-situ XPS spectra for CoMn catalysts. (A) Co 2p and (B) C 1s regions of Co_1Mn_3 catalyst under different conditions. (C) Co 2p and (D) C 1s regions of Co_1Mn_1 catalyst under different conditions. Reduction condition: H_2 , 300 °C, 5 h; Reaction condition: 250 °C, 0.1 MPa, $\text{H}_2 / \text{CO} = 1$.

generated from the Co_1Mn_3 oxides nanocomposites and stabilized on the surface of the $\text{Co}_x\text{Mn}_{1-x}\text{O}$ oxides. The size of these Co^0 clusters is too small to be observed by XRD, explaining the absence of the crystalline Co diffraction patterns in $\text{Co}_1\text{Mn}_3\text{-R}$ and $\text{Co}_1\text{Mn}_3\text{-S}$.

Previous TPR and XRD characterizations (Fig. 3) have revealed that the interaction between Co and Mn in the CoMn oxides nanocomposites is enhanced with the increase of Mn content. Consequently, we suspect that the formation of crystalline Co nanoparticles in the $\text{Co}_1\text{Mn}_3\text{-R}$ sample is not favored due to the higher Mn content. Notably, there is no signal of Co_2C in $\text{Co}_1\text{Mn}_3\text{-S}$ for the whole process even after 50 h FTS reaction, suggesting the dominant role of Co^0 cluster as the active phase in Co_1Mn_3 . de Jong et al. concluded that while $\text{Co}/\text{Mn} \approx 0.3$, the metallic Co could be well dispersed and stabilized by the MnO_x support during FTS reaction [29].

Fig. 5B shows the evolution of C 1 s spectra of the Co_1Mn_3 sample at different stages. For the fresh Co_1Mn_3 , the peaks at around 288.4 and 284.6 eV are attributed to the $\text{C}=\text{O}$ and C-C, respectively, of carbonate formed in the preparation process. After the reduction treatment, the above two peaks disappear in $\text{Co}_1\text{Mn}_3\text{-R}$. Interestingly, during the FTS reaction at 2 h, new peaks at 286.1 and 288.7 eV appear in $\text{Co}_1\text{Mn}_3\text{-S-2 h}$, ascribing to the C-O of adsorption CO molecular and $^*\text{HCOO}$ intermediate [30], respectively. This result suggests the CO adsorption and further transformation of CO on the surface of the Co_1Mn_3 catalyst. As the reaction proceeds to 50 h, the $\text{Co}_1\text{Mn}_3\text{-S-50 h}$ exhibits a small peak at 288.4 eV, corresponding to the carbonate products generated in FTS reaction. Moreover, no signal attributed to Co_2C was observed in Fig. 5A and B, confirming that the active phase of Co_1Mn_3 catalyst was Co^0 clusters rather than Co_2C .

For comparison, ex-situ XPS spectra for Co_1Mn_1 catalysts was shown in Fig. 5C and D. A peak of Co 2p at 778.0 eV appears after being reduced, indicating the formation of Co^0 on the surface of the catalyst. As the reaction time of 2 h, the Co^0 peak intensifies obviously. At 50 h, many Co_2C nanoparticles are generated, showing a strong Co^0 peak [31, 32]. The formation of Co_2C could also be verified by the C1s signal of the XPS results, where a new peak at 283.1 eV appears in $\text{Co}_1\text{Mn}_1\text{-50 h}$ that is ascribed to the carbon in Co_2C . These results show that two possible active phases exist in the Co_1Mn_1 catalyst, i.e., Co^0 and Co_2C , which is consistent with the XRD, TEM, and EXAFS results.

3.5. DFT calculation on Co^0 clusters

Density functional theory (DFT) calculations were further carried out to examine why the formation of Co^0 cluster is preferred to Co_2C in Co_1Mn_3 by calculating the carbon potential (μ), which is a descriptor for interpreting the thermodynamic feasibility of carburization of transition metals, of Co^0 cluster with different size and Co_2C . Fig. 6A shows the

critical μ values, i.e., $\mu_{\text{cri}} = E_{\text{Co}_2\text{C}} - 2E_{\text{Co}}$, to represent the minimum value to maintain the stable truncated nanoclusters ($\text{Co}_{20}\text{C}_{10}$, $\text{Co}_{48}\text{C}_{24}$, and $\text{Co}_{144}\text{C}_{72}$) and bulk Co_2C . It is observed that all the Co_2C clusters exhibit larger μ_{cri} values (> -7.33 eV) than that ($\mu_{\text{FTS}} = -8.14$ eV) in typical FTS reaction, indicating that Co_2C clusters are not stable under FTS conditions [33]. It is thus inferred that the carburization of small cobalt clusters is not favored during the FTS reactions, which is consistent with our experimental observations.

Moreover, DFT calculations were performed to understand the improved production of olefins. The reaction pathways of two consecutive hydrogenation of $\text{C}=\text{C}$ bond are illustrated in Fig. 6B. The first step of $\text{C}=\text{C}$ hydrogenation occurs easily with rate-limiting energy barrier of ca. 0.53 eV for Co_{48} cluster. However, a much higher rate-limiting barrier of ca. 1.07 eV is obtained for second step hydrogenation in the presence of sodium, resulting in significant suppression of the olefin hydrogenation.

3.6. Reaction mechanism over Co^0 clusters/ $\text{Co}_x\text{Mn}_{1-x}\text{O}$ catalyst

In traditional FTS reactions, previous studies have suggested that the active metallic Co nanoparticles could facilitate the C-C coupling reaction, resulting in high selectivity toward long-chain alkanes [34]. Interestingly, our Co_1Mn_3 catalyst shows a lower C_5^+ selectivity of 16.5%, with a chain growth factor (α) of only 0.43. The ASF plot of the product distribution over Co_1Mn_3 catalyst is presented in Fig. 7A, showing that the distribution of the CH_x species still obeys the probabilistic polymerization mechanism, but the probability of carbon chain growth drops significantly. The chain growth of the CH_x monomers species is considered to be at stepped B5 sites, which are generally composed of four atoms in the same plane and one atom in the other plane [35]. And high chain growth requires a catalyst with active phase of a certain size [36].

To confirm the size of the Co^0 clusters, we characterized the $\text{Co}_1\text{Mn}_3\text{-S}$ sample using atomic-resolution high-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Fig. 7B shows that the Co^0 clusters are 0.8–1 nm in size. These sub-nanometer sized Co^0 clusters should pose a huge steric hindrance for the C-C coupling process, resulting in a low chain growth probability as shown in Fig. 7A.

There is another important issue regarding the regulation of methane selectivity. It has been demonstrated that Co nanoparticles with smaller size are more likely to generate methane [21]. de Jong et al. found that when the size of Co nanoparticles is smaller than 3.0 nm, the methane selectivity could reach as high as 53.0%, due to the higher H coverage and lower CO coverage on the surface of small Co nanoparticles [37]. However, for the Co^0 clusters with sub-nanometer size in this study, the

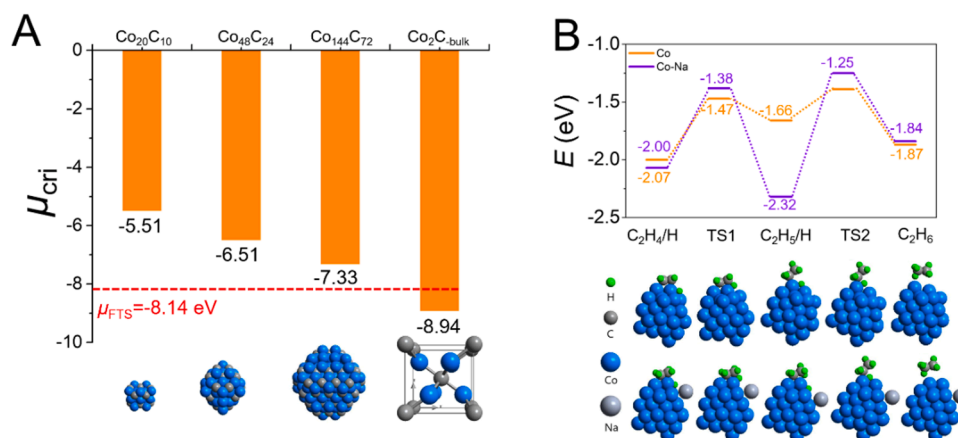


Fig. 6. DFT calculations on the catalytic behavior of Co clusters. (A) The critical carbon potential of Co_2C clusters and bulk predicted by DFT calculations. (B) The reaction pathways of two consecutive hydrogenation of $\text{C}=\text{C}$ bond on Co and Co-Na.

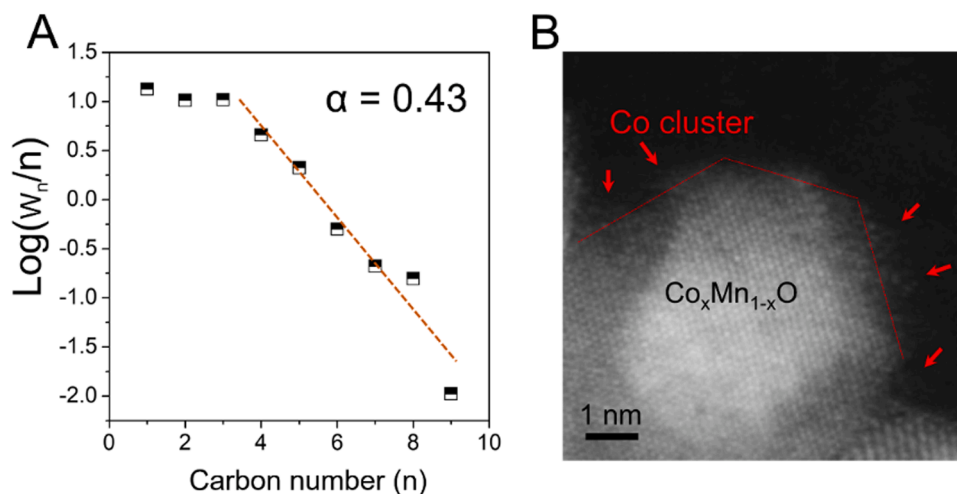


Fig. 7. Catalytic performance and structure characterization for Co_1Mn_3 catalyst. (A) Anderson-Schulz-Flory (ASF) plot of hydrocarbon products over Co_1Mn_3 catalyst. (B) Atomic-resolution high-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of spent Co_1Mn_3 -S catalyst.

methane selectivity is below to 13.5% even at a high reaction temperature of 250 °C and the lower olefins selectivity reaches 65.4% with the overall O/P ratio as high as 13.9. These results reveal that the H coverage on the Co^0 clusters has been greatly improved and the hydrogenation process has been inhibited. This is closely related to the unique electronic environment of the Co_1Mn_3 catalyst surface. Due to the unique surrounding Mn environments, these active Co^0 clusters could facilitate the adsorption of CO and inhibit the hydrogenation reaction, favoring the olefins production [29].

Results from the ex-situ Mn 2p XPS spectra (Fig. S9) further reveal the electron-rich status of the catalyst surface. In the fresh Co_1Mn_3 sample, the main valance states of Mn are +3/+4 with a peak centered at 642.1 eV, due to the partial oxidation of the catalyst surface during sample preparation [38]. After the reduction treatment, the Mn 2p_{3/2} peak in Co_1Mn_3 -R shifts to 640.3 eV, indicating that the valance states of Mn is +2 [39]. During the FTO reaction, Co_1Mn_3 -S-2 h sample shows a shift of the peak to higher binding energy of 640.6 eV, which continues to increase to 640.8 eV in Co_1Mn_3 -S-50 h. These results suggest a continuous loss of electron of the Mn atoms during the FTS reaction. These donated electrons from Mn could effectively reduce the H_2 coverage on the catalyst surface and suppress the hydrogenation reaction of olefins [40].

Notably, the role of Na promoter is also key to the high selectivity towards lower olefins and relatively low selectivity towards methane of the Co_1Mn_3 catalyst. We further verified this point by carrying out H_2 -TPD experiments. Fig. S10 shows that the Na modification greatly decreases the amount of H_2 desorption by the Co_1Mn_3 catalyst from 598.6 mmol/g_{cat} (before Na modification) to 507 mmol/g_{cat} (after Na modification). This result indicates that the Na modification could greatly inhibit the adsorption of H_2 and thus promote the adsorption of CO, resulting in a higher O/P ratio in the overall product. Moreover, the Na promoter, which acts as an electronic donor to cobalt clusters, would accelerate lower olefins desorption and also suppresses the secondary hydrogenation of olefins [23]. Therefore, the smaller particle size and low H coverage of Co^0 clusters result in a low α value and a higher O/P ratio, rendering the Co_1Mn_3 catalyst to achieve a selectivity of 65.4% for lower olefins.

More importantly, the Co^0 cluster has a low activity to catalyze water-gas shift reaction, resulting in minimum formation of CO_2 . The conversion of syngas using the Co^0 clusters/ $\text{Co}_x\text{Mn}_{1-x}\text{O}$ catalyst toward highly selectively formation of lower olefins while suppressing the formation of CO_2 are illustrated in Fig. 8. Our experimental and theoretical results conclude that the formation of stable Co^0 clusters on the surface of $\text{Co}_x\text{Mn}_{1-x}\text{O}$ nanocomposite is key to the superior selectivity toward

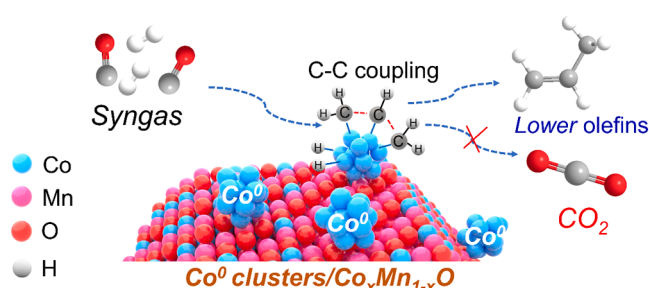


Fig. 8. Catalytic reaction mechanism for syngas conversion. Illustration of the reaction of syngas conversion to lower olefins over Co^0 clusters/ $\text{Co}_x\text{Mn}_{1-x}\text{O}$ catalyst.

lower olefins, while exhibiting remarkably low CO_2 selectivity in FTS reactions.

4. Conclusions

It is of paramount importance to improve the selectivity toward light olefins while reducing the formation of CO_2 and methane as much as possible in FTS reactions, achieving efficient carbon utilization. Current efforts have been challenged by the high CO_2 formation, which detracts the overall carbon usage. In this study, we report a CoMn oxide nanocomposite, namely Co_1Mn_3 , with a remarkably high $\text{C}_2^--\text{C}_4^--$ selectivity of 65.4% and an extremely low CO_2 selectivity of only 13.7%. Taking the generated CO_2 into account, the overall carbon selectivity toward lower olefins $\sim 60\%$. This sample also exhibits excellent stability during a continuous FTS reaction for 90 h. Results from a comprehensive set of experimental and theoretical experiments reveal that metallic Co^0 clusters are generated on the surface of the catalyst due to the reduction treatment. These Co^0 clusters are thermodynamically more stable than Co_2C , which has been suggested to be the active phase in FTO in previous studies. The Co^0 cluster rather than Co_2C as active phase facilitates the formation of lower olefins while inhibiting the formation of CO_2 , rendering the unprecedentedly high carbon usage toward lower olefins. This work provides a new mechanistic understanding on the manipulation of the active phase of Co-based catalysts for improving the selectivity toward desirable products at high carbon usage.

Funding

This work was supported by the National Natural Science Foundation

of China (No. 22072184, 22102220, and 21972170), the Young Top-notch Talent Cultivation Program of Hubei Province.

CRediT authorship contribution statement

Shuai Lyu: Methodology, Investigation, Writing - original draft. **Qingsen Wu:** Investigation, Methodology. **Zhe Li:** Investigation, Visualization. **Yuhua Zhang:** Investigation, Methodology. **Jinlin Li:** Conceptualization, Funding acquisition, Validation. **Li Wang:** Supervision, Conceptualization, Funding acquisition, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.122347](https://doi.org/10.1016/j.apcatb.2022.122347).

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